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Working with organic peroxides in the academic lab

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The author has no formal training in chemical safety; the following guide is based upon more than two decades of academic lab work with organic peroxides. Suggestions or corrections are welcomed at pdussault1@unl.edu.

ABSTRACT: The following is a brief introduction to peroxide safety from the viewpoint of a synthetic chemist. Major topics include: classes of organic peroxides; peroxide reactivity; hazard identification and minimization; reaction monitoring; and, hazards associated with auto-oxidation of peroxidizable solvents.

KEYWORDS: peroxide, hydroperoxide, hydroperoxyacetal, ozonide, perester, dihydroperoxide, monoperoxyacetal, active oxygen, peroxide strips, TLC indicator, self-accelerating decomposition, radical, exothermicity, transition metals.

CONTENTS:

1. Resources

A selection of reviews or monographs related to organic peroxides and/or peroxide reactivity are

described here; some references focused on peroxide safety are found within individual sections of this document. Readers noting the omission of a favorite review our source are encouraged to send suggestions to the e-mail listed on the first page.

Swern's three-volume series on organic peroxides, although dated, remains an excellent resource.[1] A 1988 offering in the Houben-Weyl *Methoden* series (forerunner of *Science of Synthesis)* provides a comprehensive introduction into peroxides and their reactions.[2] Multiple volumes of the Patai *Functional Group* series address peroxides.[3] A major technical encyclopedia includes an informative chapter on organic peroxides.[4] Several references are provided related to peroxide reactivity and the hazardous materials literature.[5, 6]

Suppliers of organic peroxides offer very useful information, much of it safety-related, on their web sites.[7,8,9,10] The Organic Peroxide Producers Safety Division, a plastics-related trade organization that includes the suppliers described above, also maintains a web site offering a number of useful links and documents.[11]

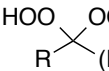
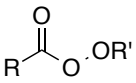
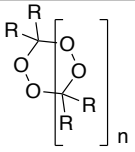
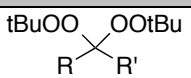
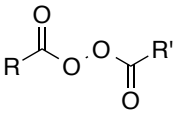
2. Major Classes of Peroxides.

Some common peroxide classes are illustrated in Figure 1, along with some general information (often representing typical ranges within the class) about typical self-accelerating decomposition temperatures (SADT)[12] and idea of thermal stability.[13,, 14, 15] Web-published guides from major vendors, while limited to commercially available material, can be useful in assessing thermal stability by and within class.[7b, 8]

3. Why are peroxides so reactive?

The O-O bond dissociation energies of peroxides, which fall in the 30-40 kcal/mol, are much weaker than O-H (>105), C-O (80-85), and C=O pi (80-85) bonds. While behavior can vary widely even within classes, particularly with changes in active oxygen content (see below), a general observation is that peroxide decompositions are often highly exothermic and proceed with a low activation barrier. As a result, experimenters must always be aware of the potential for self-accelerating and exothermic processes. Peroxides have been described as presenting greater handling risk than commercial explosives.[16] A review describing hazards of commercially available peroxides and peroxide-containing compositions towards detonation, deflagration, or fire is dated but still informative.[17]

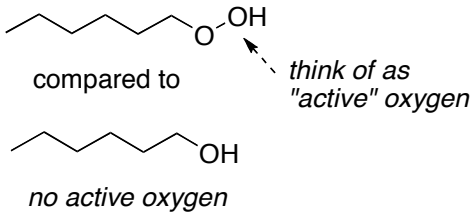
Figure 1. Common classes of organic peroxides

Class							
	Alkyl hydroperoxide		dialkyl peroxide		peracid		ozonide
Common example	*t*-BuOOH SADT 88 °C (70% aq.)		t-BuOO*t*Bu SADT 80 °C (neat)		peracetic acid SADT 55°C (as dilute soln)		*Usually less stable than bisperoxyacetal*
Temperature for 10 hr half-life	133-172 °C		117-133 °C		stability varies widely with structure and formulation		
Class							
	gem or 1,1-dihydroperoxide		cyclic peroxide, ~endoperoxide		peresters		cyclic ketone peroxides
Common example	1,1-dihydroperoxy cyclohexane		-		t-butyl perbenzoate SADT 63 °C (neat)		3,6,9-Triethyl-3,6,9-trimethyl-1,4,7-triperoxonane; SADT 125 °C
Temperature for 10 hr half-life	-		-		varies with structure: 49-107 °C		90-110 °C (listed example is 115 when dissolved in oil
Class							
	hydroperoxyacetal		bisperoxyacetal		acyl peroxide		
Common example a	-		1,1-di-t-butyl peroxycyclohexane		benzoyl peroxide SADT 68 °C (solid)		
typical temp, 10 hr half-life	-		92-115 °C		20-75°C		

4. Determination of reactivity and minimization of hazard. [11,15,17,18]

Steps to take before an experiment (or before scaling up):

Determine active oxygen content. "Active" oxygen (A.O.) content refers to the mass fraction of the active, or peroxide, oxygen.[11] For example, hydrogen peroxide (H_2O_2) and water (H_2O) have 47% and 0% A.O., respectively. Low A.O. does not *guarantee* safety (more on this below) but a high value alerts you to possible danger. For example, MeOOH (33% A.O.) can spontaneously detonate, while octyl hydroperoxide (11% A.O.) is easily handled in small amounts. *A rough guideline:* Try to work with organic peroxides in which the nonperoxidic portion of the molecule has at least six carbons (or the equivalent mass). We make exceptions to this only for molecules whose behavior is well established, for example, t-butyl hydroperoxide.



Active Oxygen (A.O.) as an approximate guideline for precautions

≤ 5%: *Example: A C18 fatty acid hydroperoxide*. Usually safe. Normal precautions unless special factors (e.g., very large scale)

5-10%: *Example: benzoyl peroxide*. Caution warranted when: multigram scale; known issues with the substrate class; reaction will involve heating concentrated solutions of peroxides or exposing concentrated solutions to redox-active transition metals.

10-15%: *Examples: many peracids, ozonides of C_5-C_8 alkenes.* Caution warranted even on gram scale. On multigram scale, consider use of shields or more formal protective devices. Consider preliminary thermal analysis on large scale. Cumene hydroperoxide, a relatively "tame" hydroperoxide on laboratory scale, offers an instructive example.[19]

>15%: *Examples: "acetone peroxides", ozonides of < 5C, peracetic acid*. Assume the material may detonate or deflagrate without warning. For example, 2-methoxyprop-2-yl hydroperoxide (A.O. ~15%),[20] a reagent developed in our lab and used by others without event, has nonetheless been observed to deflagrate on a scale of 10-20 mmol.

Dilution (with a material inert to the peroxide) effectively lowers active oxygen and the risk of SADT. For example, peracetic acid cannot be sold as a pure material but can be sold and transported as 30-40% solutions.

Look for literature on the molecule or close relatives: Has this or a similar molecule been reported to explode or undergo violent decomposition?[18] Structure is important. *tert*-Butyl hydroperoxide (18% active oxygen) is generally stable on moderate scale unless "provoked" (see below) while triacetone triperoxide (A.O. ~ 20%) is an easily detonated (friction, heat, spark, shock) high explosive.[21] The CAMEO Chemicals database, supported by the US National Oceanographic and Atmospheric Administration (NOAA), includes a substantial grouping of safety sheets for organic peroxides.[22] References to temperature dependent half-lives of several classes of common peroxides are provided. [4, 7, 8, 23]

Conduct thermal analysis: Once you have some initial examples of a target, thermal data is easily obtained using a scanning calorimeter (DSC or DSC/TGA). Pay attention to the onset of decomposition and the amount of heat released.[24] References to examples of thermal analysis are provided. [25,26]

Minimizing Danger During Reactions

Minimize scale: Reactions of peroxides are often associated with substantial exothermicity. For example, a formal 2 $H^+/2e^-$ reduction of H_2O_2 is associated with an enthalpy change of approximately 75 kcal/mole. Particularly with low molecular weight peroxides (this includes concentrated solutions of H_2O_2!), minimize scale. An explosion on 1-2 mmol may result in a good "lab" story; an explosion on multigram scales can produce serious injury. This point is valid even with some familiar peroxides. Benzoyl peroxide (A.O. < 7%), a common initiator used in both academic and industrial settings, undergoes auto ignition at 80 °C and has been known to explode violently upon exposure to heat, friction, or flammable organics.[6,27]

Distance/Protection: An explosion at the end of a clamp, or better yet, behind a shield, is better than one in the hand.

Avoid provoking decomposition reactions:

- If you must heat peroxides and do not have experience or literature evidence for thermal stability, conduct an initial calorimetric survey (see above) and/or take extra safety precautions (distance, shield).
- Be very careful about storing, transporting, or heating relatively reactive peroxides (peracids, hydroperoxides, 1,1-dihydroperoxides, peresters) in the presence of oxidizable solvents or materials (wood, paper).

•Be very cautious in exposing hydroperoxides, dihydroperoxides, peracids, peresters, diacyl peroxides, or ozonides to redox active metals (for example: Cr, W, Mn, Fe, Cu, Ni, among others). This concern is obviously greatest for neat samples or concentrated solutions of high A.O. and is minimal for small amounts of *unstrained* dialkyl peroxides; however, caution is nonetheless called for, particular for reactions on large scales or involving high concentrations.

Never allow redox-active metals or metal tools (spatula, needle) to come into contact stock or concentrated solutions of H_2O_2 or tBuOOH. [28] A best practice, especially on large scale, is to use Teflon needles/plastic syringes for liquid transfers and Teflon, glass, or polyethylene scoops for solid transfers. In a pinch, one can place a minimal amount of the reagent into a glass vial and syringe from this.

•A number of peroxides can decompose violently in the presence of strong acids.[29]

•Fe(II) salts react with even hindered peroxides to generate reactive radicals. In the case of strained peroxides, even traces of ferrous iron can lead to exothermic decomposition.[30]

•Hydrogen peroxide or low molecular weight hydroperoxides (e.g., tBuOOH) should be washed out of reaction mixtures prior to concentration.

H_2O_2 will generally wash out with water. Small molecular weight hydroperoxides (pKa ~ 12) can be washed out with very strong base (e.g. 4N NaOH).

A final rinse with sulfite or bisulfite will remove most remaining hydroperoxides but will not attack dialkyl peroxides and will rarely attack ozonides.

The removal of hydrogen peroxide or hydroperoxides can be monitored using peroxide indicator strips or the redox-active indicator (both discussed below).

• Reduction of dialkyl peroxides and related species (e.g., bisperoxyacetals) will require stronger reducing agents such as triphenyl phosphine or Zn/HOAc.[31]

•Procedures for decomposition of ozonides are summarized in a recent review.[32]

Monitoring reactions:

Overview: An older but still useful monograph contains many useful methods for analysis and titration/quantification of organic peroxides;[33] a more truncated set of information can be found in the *Methoden* review.[2]

TLC: The formation or loss of peroxides is easily monitored using a TLC dip based upon

N,N'-dimethyl-*p*-phenylenediamine.[34] Unhindered ozonides, hydroperoxides, peracids, and hydroperoxyacetals give a dark magenta color upon dipping; less reactive dialkyl or alkyl/silyl peroxides will generally show a color change only after heating.

Peroxide test strips: Commercially available colorimetric indicators, while designed to quantitate H_2O_2 in aqueous media, can be employed for reasonably accurate determination of the concentration of H_2O_2 or alkyl hydroperoxides in ethereal solvents or alcohols.[35] For low-boiling solvents, place a drop or two of the sample to be tested on the indicating pad, and blow (exhale) across the pad to remove solvent and supply necessary moisture. See http://www.sigmaaldrich.com/chemistry/solvents/learning-center/peroxide-formation.html

Isolated peroxides. Working with isolated peroxides requires additional care; there is no solvent to slow reaction rate and buffer temperature rise. Crystalline peroxides should be regarded as **particularly dangerous**. If you unexpectedly isolate a crystalline peroxide, particularly if high A. O. content, put the sample behind a shield and try to get it back into solution without a If you must work with crystalline peroxides, test a small amount for shock sensitivity as follows. Using a plastic or glass spatula, carefully place 10-15 mg on some weighing paper, place the folded paper on a concrete surface, and then tap it with a hammer. In our experience, an obvious reaction (pop, or flame) is sign of a highly shock-sensitive peroxide. Do not subject crystalline peroxides to friction (spatula, screw top of a vial) or expose to any metal implements (use a porcelain or Teflon spatula). Avoid mixtures of low molecular ketones, acids, and hydrogen peroxide, which can readily produce crystalline 1,2,4,5-tetraoxanes, 1,2,4,5,7,8-hexaoxanonanes, and polymeric peroxides. Hydrogen peroxide should never be used in ketone solvents or stored in the presence of aliphatic ketones or almost any aldehydes.[36,37, 38]

5. Toxicity.

Some classes of peroxides have significant exposure risks. Avoid breathing high concentrations of vapors from volatile peroxides. This includes odorless H_2O_2, which is considered to hold immediate danger to life and health (IDLH) at 75 ppm. [39] Reactive peroxides are destructive to biological tissues and ingestion or contact, particularly with the eye,[40] must be avoided.[41] For example, peracetic acid, a common industrial and sanitizing chemical, carries serious GHS hazard categories for skin corrosion (1) and eye damage (1A),[42] and a recommended limit for prolonged exposure of only 0.17 ppm.[43] Hydroperoxides

are relatively irritating.[11] Some peroxides have shown activity as tumor promoters in a mouse skin model.[44]

6. Peroxidizable substrates (auto-oxidation).

The spontaneous generation of peroxides from oxidation of organics under air, often described as auto-oxidation, is a significant, but easily preventable, hazard. The usual rate-limiting step, abstraction of a hydrogen atom by a peroxyl radical, is most favorable for substrates where the derived carbon radical is allylic or benzylic (cumene, ethyl benzene) or else substituted by a neighboring ether oxygen or amide nitrogen (e.g., THF, ether). The following references identify common materials susceptible to peroxide formation. [18,35, 45,46]

Even if autoxidation does occur, the resulting solutions are rarely dangerous to handle unless the peroxides precipitate as crystals (common for diisopropyl ether) or when the solutions are concentrated. The latter is a common problem for aged solutions of THF or ether; evaporation or distillation concentrates the higher boiling hydroperoxide to levels where violent explosions occur without warning.

> In an incident from my own department, an attempt to distill approximately four liters of aged tetrahydrofuran (THF) under air and in the absence of any effective reducing agent resulted in an explosion that was so violent that some portion of the apparatus was ejected through the hood sash, injuring the experimenter.

Testing: Test older supplies with the peroxide test strips (above). If the stock solvent (for example, ether or THF) shows any significant blue coloration, you should consider either: purifying the solvent from a still that will decompose peroxides (for example Na/benzophenone under N_2 or Ar) or disposing of the solvent.

Prevention: Date containers of peroxidizable solvents (examples: ether, THF, 1,4-dioxane, cumene) upon opening. If a significant period of time has elapsed since the can or bottle was first opened (my university recommends six months) the solvent should be checked before use (see testing-previous paragraph). Avoid storage of peroxidizable solvents in clear bottles. Avoid having a headspace of air; if you must store ethereal solvents under a significant headspace, consider blanketing with some nitrogen or argon.

7. Handling and transport.

Guidelines for handling of peroxides are provided from both academic and industrial sources.[7,11,47] Lead references are provided for issues related to transport of organic peroxides,[48] and to spill cleanup.[49] Note that nearly all peroxides are considered hazardous materials for shipment by air and that a number of reactive peroxides may require special handling (refrigerated transport) packaging or formulation (e.g., presence of diluents) for ground transport.

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[11] http://www.plasticsindustry.org/supply-chain/material-suppliers/organic-peroxide-producers-safety-division-oppsd (Accessed August 2018)

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